

ELECTRON DIFFRACTION DETERMINATION OF AN ORIENTATION-RELATIONSHIP FOR IRIIDIUM-ON- η -ALUMINA

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Received 23 July 1990; accepted 13 September 1990

Ignition catalyst, Ir/Al₂O₃, nucleation, electron diffraction, Shell 405 catalyst, hydrazine

An iridium-on-alumina catalyst used for the spontaneous ignition of the decomposition of hydrazine in spacecraft position control thrusters exhibits nearly complete matching of the selected area electron diffraction patterns in the [110] orientation for iridium crystallites and for the support η -alumina. The orientation-relationship is referred to the porous character of the η -alumina skeleton favoring an oriented nucleation and growth of iridium crystallites in the pore mouths.

Transition aluminas are widely used as supports for highly dispersed metal catalysts [1]. An iridium-on- η -alumina catalyst (Shell 405) has turned out to have superior properties for hydrazine decomposition in spacecraft position control thrusters with respect to spontaneous ignition and long-term stability [2]. The high dispersion of the iridium metal phase, even on a crystalline form of η -alumina, was related to a strong metal-support interaction concluded from a corresponding shift of the iridium X.p.s. signals [3]. Strong metal-support interactions (SMSI) frequently exist [4] and electron microscopy has proved to be a powerful tool for the identification of peculiar kinds of SMSI [5]. In the following, electron optics are used for the analysis of an iridium-on-alumina catalyst (Shell 405, 20–30 mesh, 32 wt.% Ir).

Samples for electron microscopy (Philips 420 T. LaB₆ cathode, 120 kV) were prepared by ultrasonic disaggregation of the catalyst pellets and sprinkling of a butanol suspension onto carbon films supported by copper grids.

The transmission electron micrographs show a high fraction of crystalline support having mean crystal sizes around 0.1 μ m (fig. 1a). Phase contrasts of array structure, having spacings around 3.5 nm, are observed (fig. 1b). Selected area electron diffraction obtained along the [110] zone axis on the crystalline domain of the support gives the pattern characteristic for a cubic structure (fig. 2a). For many reflexes the intensities show a non-centrosymmetric distribution. This effect can be related to the slight mismatch of reflexions originating from the

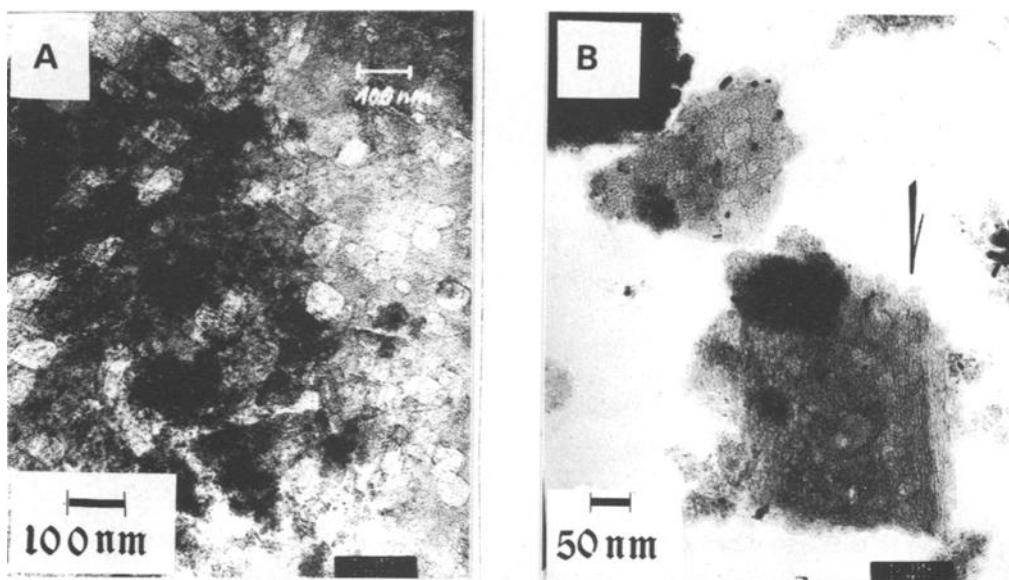


Fig. 1. Transmission electron micrographs of the Ir/ η -Al₂O₃ catalyst showing large (0.1 μ m) carrier crystals (A) and phase contrasts of array structure (B).

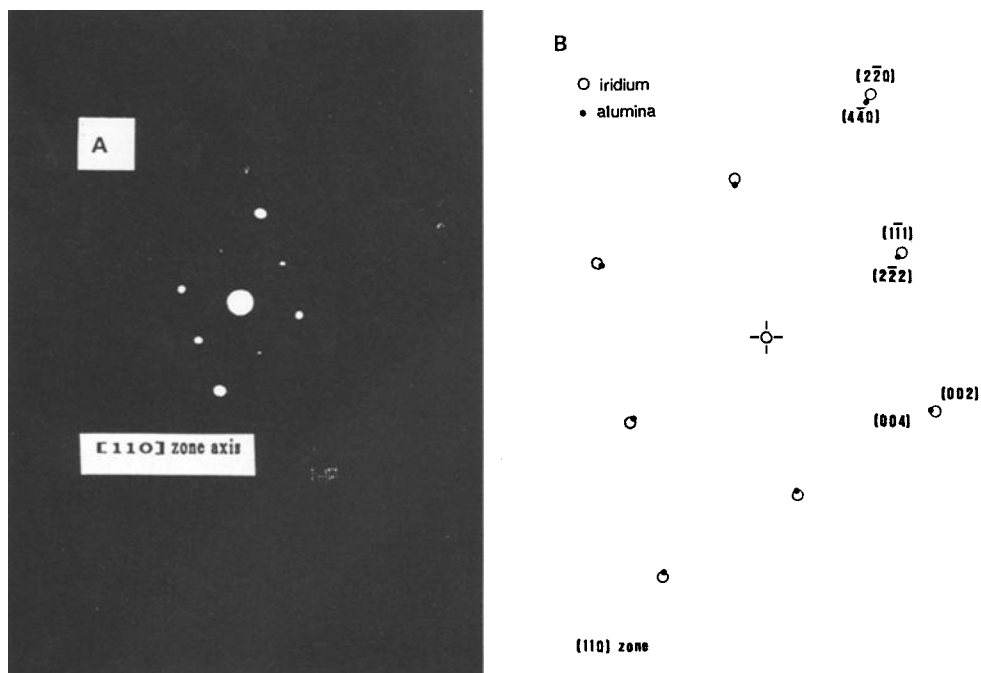


Fig. 2. (A) Selected area electron diffraction from crystalline domains of the support. (B) Indices of diffraction pattern.

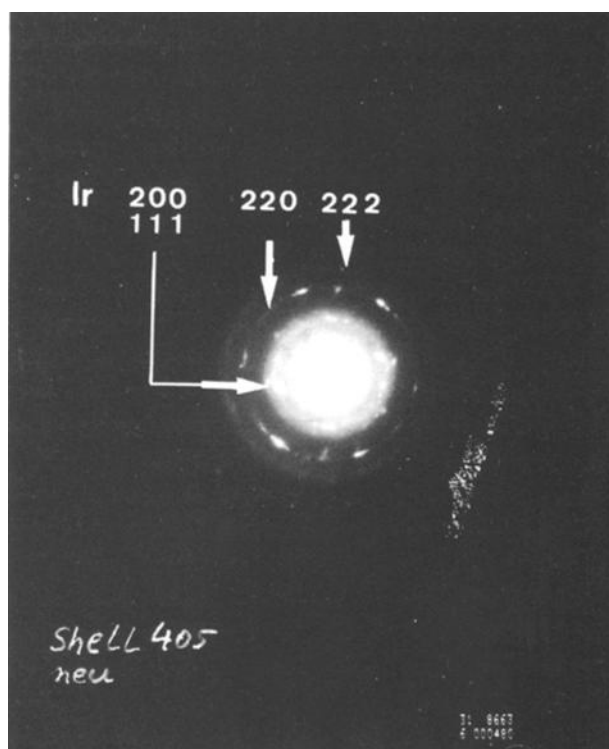


Fig. 3. Selected area electron diffraction from amorphous domains of the support, showing diffraction rings of the fcc Ir.

face centered cubic η -alumina and the face centered cubic iridium (fig. 2b), e.g. showing deviations of 2% for the positions of the [400] reflexion of η -Al₂O₃ and of the [200] reflexion of Ir in the X-ray diffraction diagrams [6]. It is highly probable, that the scattered reflexes originate from the iridium crystallites, whereas the intense spots have to be related to the relatively large η -Al₂O₃ crystals. The presence of γ -phase alumina could be excluded by X-ray diffraction giving no indication for the characteristic splitting of the [440] reflexion [7].

The scattered nature of the iridium reflexions has to be related to the small size of the iridium crystallites, i.e. an average iridium particle size around 2 nm is obtained from oxygen chemisorption giving 190 m²/g Ir for the fresh and 140 m²/g Ir for the used (10^4 WHSV {g N₂H₄/g[cat] · h}) catalyst. A few larger Ir crystals are found on the amorphous fraction of the alumina support giving diffraction rings, i.e. random orientation, in the selected area electron diffraction graphs (fig. 3). The amorphous fraction might contribute by one quarter to one third to the total amount of support comparing the measured BET surface area of 90 m²/g to average values around 200 m²/g being valid for amorphous alumina [8].

The missing of random orientation for the Ir crystallites on the crystalline η -alumina or the orientation-relationship between metal and support, respectively, might be referred to structural peculiarities of the carrier. The η -alumina contains slit-shaped pores with a width around 1 nm normal to the (111) plane [7] being responsible for the lamellar structure at the surface (fig. 1b). The spacing of 3.5 nm between the lamellae exceeds the value expected for a (111) face but fits for a (110) face. The exposition of (110) planes at the surface of η -alumina crystals is often established [9]. Under the assumption that the impregnation procedure favors accumulation, nucleation and growth of Ir crystallites in the pore mouths, the orientation-relationship can be referred to a structural accommodation of the fcc metal guest in the pore mouths of the fcc host, as was observed for zeolite accommodated Pt crystallites [10].

The outstanding properties of the Shell 405 catalyst are, presumably, mainly based on the presence of a high fraction of η -alumina crystals, stuck together by amorphous alumina binder. The dense crystals prevent penetration of hydrazine into the interior of the pellets, and, thus decreases the possibility of generation of catalyst fines via breakup processes from internal overpressure. The lamellar skeleton of the η -alumina reduces the rate of phase transition [7] and, thus, increases the thermal stability.

Acknowledgement

The authors gratefully acknowledge material and know-how supply by the MBB/ERNO Spacecraft Corporation, financial support by the Senator für Bildung, Wissenschaft und Kunst der Freien Hansestadt Bremen, production of electron micrographs by Dr. A. Kleine and valuable discussions and comments by Drs. H. Kral and R. Lamber.

References

- [1] a) B.C. Lippens and J.J. Steggerda, in: *Physical and Chemical Aspects of Adsorbents and Catalysts*, (ed. B.G. Linsen) (Academic Press, New York, 1970);
b) B.C. Gates, J.R. Katzer and G.C.A. Schuit, *Chemistry of Catalytic Processes*, (McGraw-Hill, New York, 1979).
- [2] a) E.W. Armstrong, B.L. Ryland and H.H. Voge, Shell, Houston, TX, Patent DE 2835629 (1980);
b) E.W. Schmidt, *Hydrazine and its Derivatives – Preparation, Properties, Application*, (Wiley, New York, 1984).
- [3] J. Escard, C. Leclerc and J.P. Contour, J. Catal. 29 (1973) 31.
- [4] a) G.C. Bond and R. Burch, *Catalysis – A Specialist Periodical Report*, The Royal Society of Chemistry, London 1983, vol. 6, p. 27.
b) *Metal Support Interactions in Catalysis, Sintering and Redispersion* S.A. Stevenson, J.A. Dumesic, R.T.A. Baker and E. Ruckenstein, Eds., (Van Nostrand/Reinhold, New York, 1987).

- [5] a) R. Lamber and W. Romanowski, J. Catal. 105 (1987);
b) R. Lamber, N. Jaeger and G. Schulz-Ekloff, J. Catal. 123 (1990) 285.
- [6] Powder Diffraction File, Joint Committee on Powder Diffraction, International Center for Diffraction Data, Swathmore, PA, 1979; η -Al₂O₃: Card 4-0875, Ir: Card 6-0589.
- [7] B.C. Lippens and J.H. de Boer, Acta Cryst. 17 (1964) 1312.
- [8] H. Kral, Chemiker Ztg./Chem. Apparatur 90 (1966) 235.
- [9] a) H. Knözinger and P. Ratnasamy, Catal. Rev.-Sci. Eng. 17 (1978) 31;
b) A. Reller and d.L. Cocke, Catalysis Letters 2 (1989) 91.
- [10] A. Kleine, P.L. Ryder, N. Jaeger and G. Schulz-Ekloff, J. Chem. Soc., Faraday Trans. 1, 82 (1986) 205.